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EFFECT OF TEMPERATURE ON WATER VAPOR TRANSPORT THROUGH POLYMER MEMBRANE LAMINATES

by
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This report determines the extent to which the water vapor transport properties of nine different polymer membranes and membrane/textile laminates are affected by temperature. A particular test method, the Dynamic Moisture Permeation Cell (DMPC), is ideally suited for this type of study, due to its complete control over the humidity and gas flow rate on the two sides of the test sample, and the ability to control the temperature of the test system. This allows temperature-dependent effects to be separated from concentration-dependent effects on mass transfer phenomena. The DMPC permits the experimenter to explore the temperature dependence of the diffusion behavior at different points on the vapor sorption isotherm of the hydrophilic polymer component of a polymer film or membrane laminate. Temperature effects are shown to be much less important than concentration-dependent effects in a hydrophilic polymer layer. Observed changes in water vapor flux at different temperatures are primarily due to the relationship between temperature and the saturation vapor pressure of water, and not to intrinsic changes in polymer permeability.

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MASS TRANSFER	SORPTION	POLYMERS	LAMINATES
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DIFFUSION	TEMPERATURE	MEMBRANES	WATER VAPOR TRANSPORT

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PREFACE

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Through Polymer Membrane Laminates

1.   Introduction

Polymer membranes laminated to textiles are used extensively in waterproof breathable clothing items such as jackets, gloves, and boots. The polymer membrane acts as a barrier to liquid water entry from the environment, but is sufficiently permeable to water vapor to allow significant amounts of sweat to evaporate through the clothing system. Familiar examples are Gore-Tex® and Sympatex® clothing products.

Laboratory testing is usually a necessary first step to evaluate the comparative water vapor transport properties of candidate materials for new clothing system designs. However, comparison of material properties often becomes complex due to changes in tested properties at different test conditions. One material may be rated better than another material at one particular set of test parameters, yet the ranking may reverse under a different set of conditions. The two effects which are usually responsible for changes in ranking of materials are concentration-dependent permeability, and temperature-dependent permeability.

Concentration-Dependent Permeability -- Membranes which contain a continuous hydrophilic component, such as Gore-Tex® and Sympatex®, change their transport properties based on the amount of water contained in the hydrophilic polymer layer. The magnitude of the relative changes in water vapor transfer rate as a function of membrane water content are quite large for several common clothing materials and systems. The water content of these materials is a function of the water vapor content (humidity) of the environment on either side of the clothing layer. Test methods which evaluate concentration-dependent permeability need to be capable of independently varying the relative humidity of the environment on the two sides of the material. Concentration-dependent permeability has been studied and reported on extensively [1-5]. Reported work on measured temperature-dependent water vapor transport properties of clothing membrane laminates is less common [6].

Temperature-Dependent Permeability -- Some polymer membranes may exhibit lower intrinsic water vapor transfer properties at low temperatures. This effect is of practical importance for the ability of cold weather clothing to dissipate water vapor during active wear, or for boots, gloves, and sleeping bags to dry out under cold conditions. Knowledge of temperature-dependent permeability is also important when comparing test results between test methods or laboratories which may conduct standard testing at different temperatures. Analysis of temperature-dependent permeability must distinguish between changes in the intrinsic transport properties of the material, and the apparent decrease in water vapor transport rates due simply to the lower vapor pressure of water at lower temperatures.

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Osczevski [6] has shown that water vapor diffusion in hydrophilic films and membranes can be affected by the ambient temperature. The intrinsic water vapor diffusion resistance increases at lower temperatures, which lowers the rate at which water vapor is transported across the layer.
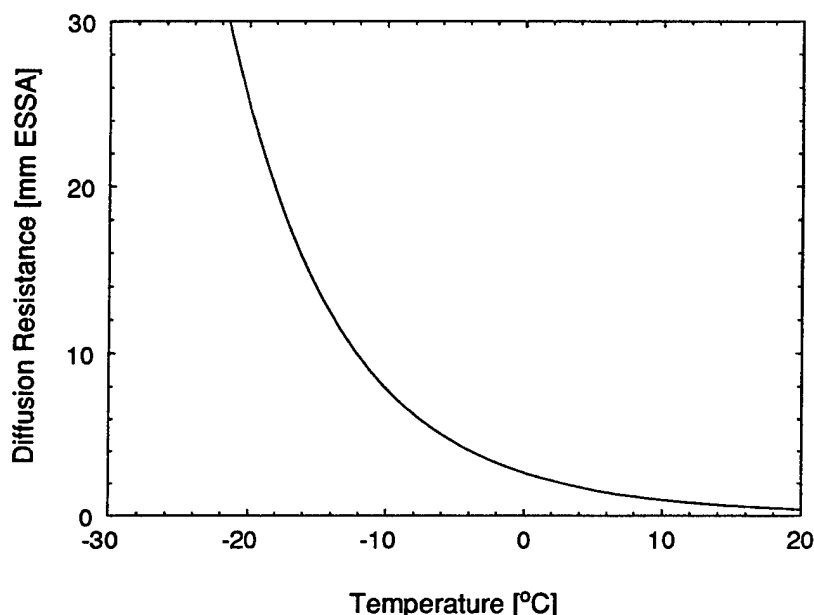
Figure 1. Change in Water Vapor Diffusion Resistance of a Hydrophilic Membrane due to Temperature (Redrawn from Osczevski [6]).

It is difficult to evaluate temperature-dependent permeability with common textile test methods. The method used by Oscevski was a modified cup method which could not independently control the humidity on the two sides of the sample. Thus the temperature-dependent results obtained by Oscevski were not obtained at similar polymer water content levels (or equivalent points on the water vapor sorption isotherm). This means that the water vapor transport results were also affected by the concentration-dependent transport properties of the materials which were tested.

The objective of this study is to determine the degree to which water vapor transport properties of several different polymer membranes and membrane/textile laminates are affected by temperature. A particular test method, the Dynamic Moisture Permeation Cell (DMPC), is ideally suited for this type of study, due to its complete control over the humidity and flow rate on the two sides of the test sample, and the ability to control the temperature of the test system. This allows temperature-dependent effects to be separated from concentration-dependent effects on mass transfer phenomena. The DMPC permits the experimenter to explore the temperature dependence of the diffusion behavior at different points on the vapor sorption isotherm of the hydrophilic polymer component of a polymer film or membrane laminate.

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2. Materials and Methods

Materials

Nine materials were selected for testing under various conditions. The materials are all polymer membranes or membrane laminates. These materials are of interest for various types of protective clothing systems. They include commercially available polymer membrane/fabric laminates used in items such as gloves, boots, and cold weather parkas. Some of the materials are under development for chemical protective clothing applications and the composition of the membrane component is proprietary.

Material Designations and Description

Sample Designation	Description
Microporous PTFE Membrane	A microporous polytetrafluoroethylene (PTFE) membrane. This membrane is typically laminated to a textile fabric to produce a clothing layer that is quite windproof and resists liquid water penetration. This is due to the extremely small pore size and the hydrophobic surface properties of the PTFE. The membrane is very thin and porous, so that it presents very little resistance to the diffusion of water vapor through the air contained in the interconnected pores.
Perfluorosulfonate Ionomer Membrane	Commercially available ionomer membrane (Nafion® 117, DuPont). This monolithic membrane is quite hygroscopic, and the transport behavior is dependent on the amount of water contained in the polymer matrix.
PTFE/PAO/PU Membrane	This membrane is composed of an expanded PTFE membrane that has been partially infiltrated on one side with a polyalkylene-oxide (PAO) polyurethane-urea (PU) coating. The coating forms a continuous layer of a hygroscopic polymer component in the membrane. The hygroscopic polymer layer is the controlling factor in water vapor transport across the membrane. (Gore-Tex®, W.L. Gore & Associates)

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PTFE/PAO/PU Laminate	The PTFE/PAO/PU membrane which has been adhesively laminated to an outer woven nylon shell fabric and inner knit nylon fabric. (Gore-Tex®, W.L. Gore & Associates)
Polyester/Polyether Membrane	This membrane is composed of a monolithic polymer layer composed of a hygroscopic copolymer of polyester and polyether. (Sympatex®, Akzo-Nobel)
Polyester/Polyether Laminate	The polyester/polyether membrane which has been adhesively laminated to an outer woven nylon shell fabric and inner knit nylon fabric. (Sympatex®, Akzo-Nobel)
Derivatized Cellophane Membrane	A cellulosic membrane, produced from viscose, modified to prevent organic vapor transport. (composition proprietary).
Derivatized Cellophane Laminate	The derivatized cellophane membrane laminated to a textile substrate. (composition proprietary).
Chemical Protective Laminate	A membrane laminate designed to minimize organic vapor transport, while retaining adequate water vapor transfer properties. Contains hygroscopic and nonhygroscopic membrane components, laminated to an outer woven nylon fabric and inner knit nylon fabric. (composition proprietary)

Method

The Dynamic Moisture Permeation Cell (DMPC) [7-9], is an automated device that can test the mass transport properties of very small pieces of woven and nonwoven fabrics, membranes, and foams. The apparatus is more convenient to use than the traditional test methods for textiles and clothing materials, and allows one to use a wider variety of test conditions to investigate concentration-dependent and nonlinear transport behavior of the many types of semipermeable membrane laminates which are now commercially available. The DMPC has been used to characterize transient affects associated with vapor sorption, material transport property changes due to swelling effects, and transport properties of electrospun nanofiber membranes [10-13]. Results generated with the DMPC have been shown to agree with standard ISO (International Standards Organization) and ASTM (American Society for Testing and Materials) methods for steady-state testing [8].

A schematic of the DMPC apparatus is shown in Figure 2.

Voltage Outputs for Flow Control and Valve Positioning

PC with D/A Output and A/D Input

Voltage Inputs

Temperature and Humidity Analog Output (Voltage)

Thermocouples

Differential Pressure Measurement Unit

Flow Control

Flow Control

ΔP

Automated Valve to Adjust ΔP

Control Unit for Mass Flow Controllers

N$_2$ Tank or Cylinder (Dry N$_2$)

Flow Control

Flow Control

Sample

Sample Holder

Humidity Probes

Mass Flow Meter

Automated Valve to Adjust ΔP

Saturated N$_2$ Bubblers

Heat Exchanger and Fan

Insulated Chamber

Temperature-Controlled Circulating Water Bath

Figure 2. Schematic of DMPC Test Arrangement.

Nitrogen streams consisting of a mixture of dry nitrogen and water-saturated nitrogen are passed over the top and bottom surfaces of the sample. The relative humidity of these streams is varied by controlling the proportion of the saturated and the dry components. By knowing the temperature and water vapor concentration of the entering nitrogen flows, and by measuring the temperature, water vapor concentration, and flow rates of the nitrogen flows leaving the cell, one may measure the fluxes of gas and water vapor transported through the test sample.

The sample conditioning system provides control over of test temperature over the range of -15 °C to 50 °C. The humidification system based on the water bubblers is adequate for test temperatures from 0 °C (ice/water mixture) to 50 °C. For subzero temperatures, the bubblers must be replaced by flow tubes filled with ice chips. It is necessary to provide a flow path long enough for the gas to become saturated with respect to the water vapor pressure over ice at the particular test temperature. Some limited subzero testing has been carried out with this system [14], but this report focuses on temperatures above freezing.

For nonporous samples, transport of water vapor proceeds by pure diffusion, driven by vapor concentration differences. For porous materials, if a pressure difference across the sample is present, convective gas flow through the sample carries water vapor along with the flow, which may add to or subtract from the diffusive flux, depending on the direction of the convective gas flow.

The following equations for calculating water vapor flux apply to either the top or bottom flows in the cell. Strictly speaking, only one measurement on one side of the cell is necessary; the use of two separate humidity transducers for the top and bottom flows allows two measurements of water vapor flux to be made at the same time, using the equations given below for either the top or bottom flow, as appropriate.

For this type of test, the mass flow rate of water vapor diffusing through the test sample from one side of the cell to the other is given by:

$$\frac{\dot{m}}{A} = \frac{Q(\delta C)}{A} = \frac{Q(C_2 - C_1)}{A} \tag{1}$$

$\dot{m}$ mass flux of water vapor across the sample [kg/s]
A area of test sample [m²]
Q volumetric flow rate through top or bottom portion of the cell [m³/s]
δC $= C_2 - C_1$, water vapor concentration difference between incoming stream (C_1) and outgoing stream (C_2) in top or bottom portion of the moisture permeation cell [kg/m³]

The incoming water vapor concentration is determined by the ratio of the mass flows of the saturated and the dry nitrogen streams. The mass flow rates are controlled by MKS model 1259C mass flow controllers, with a Model 247C 4-Channel Readout (MKS Instruments, Inc.). These mass flow controllers can control mass flow rate at an accuracy of ±0.8% of full scale, with a response time of less than two seconds. At constant mass flow, the true volumetric flow rate will vary with temperature; the flow rate set by the MKS controllers is indicated in terms of volumetric flow rates at standard conditions of 0°C and atmospheric pressure (1.01325 x 10⁵ Pa) The actual volumetric flow rate at different temperatures may be found from the mass flow rate, the temperature, and the pressure of the actual flow.

For water vapor diffusion, the critical measurement is the outgoing flow water vapor concentration C_2, which can be measured in a variety of ways. In the work reported here, capacitance-type relative humidity probes (Vaisala HMI 32 or 38) with Type HMP 35 or 37 sensors were used (Vaisala Inc.), which are adequate for materials which have significant vapor flux across them. The advantage of these probes is that they have a relatively fast response time (5 to 30 seconds: response time slower at higher humidities), which is useful for transient studies. The probes are listed by the manufacturer as having an accuracy of ±1% from 0 to 90% relative humidity, and ±2% from 90 to 100% relative humidity.

The measurement accuracy of these probes may be improved to ±0.5% by determining a calibration curve *in situ*. This is done by placing an impermeable aluminum foil sample in the cell and varying the relative humidity of the gas flow in the top and bottom of the cell by means of the flow controllers. The resulting curves (at increments of 10% r.h.) of measured relative humidity versus true relative humidity (set by the flow controllers) are used as calibration factors to correct the measured relative humidity for subsequent tests. Sorption hysteresis of the hygroscopic polymer used in the capacitance probe make any further improvements in probe accuracy difficult. For test materials which have small vapor fluxes, requiring measurements at very low concentrations, an 1100DP Dew Point Hygrometer (General Eastern Instruments, Inc.) may be used. For the highest accuracy, various instruments such as an M200 Gas Chromatograph (MTI Analytical Instruments, Inc.), or a diode laser spectroscope [10] have also been used as the concentration measurement device, but this is much less convenient in the practical sense of a routine test.

To obtain the water vapor concentration in the outgoing air stream, one must be able to convert from the known values of relative humidity and temperature to water vapor concentration. The vapor pressure of saturated water vapor in air is obtained from an empirical formula (or tables) as a function of temperature, and then converted to concentration using the perfect gas law.

We may express the water vapor transmission rate in terms of the indicated volumetric flow rate at standard conditions, the humidity difference, and the temperature:

$$\frac{\dot{m}}{A} = \frac{\delta\phi Q_s p_s M_w}{ART_s} \tag{2}$$

M_w molecular weight of water vapor [18.015 kg/kmole]
Q_s volume flow rate at standard conditions of 0°C and atmospheric pressure [m³/s]
R universal gas constant [8314.5 N-m/kg-°K]
T_s reference temperature at standard conditions of 0°C in degrees K (273.15 K)
p_s saturation vapor pressure of water [Pa]
$\delta\phi$ $= \phi_2 - \phi_1$, relative humidity difference between incoming stream (ϕ_1)
     and outgoing stream (ϕ_2) in top or bottom portion of the moisture permeation cell
ϕ $= p_v/p_s$, relative humidity
p_v vapor pressure of water [Pa]

For the present test apparatus, various sample holders are available, which have different test sample measurement areas, and which have different downstream locations from the flow inlet. All test results given in this study used a sample measurement area of 1.0 x 10⁻³ m², and the sample was located equidistant from the inlet and outlet ports of the cell. The volumetric flow rate used was 8.33 x 10⁻⁶ m³/s (500 cm³/min). Details of the sample holder are shown in Figure 3.

Differential Pressure
Measurement Ports

Flow Inlet
or Outlet

Upper Half of Flow Cell
(Identical to Lower Half)

Measurement Area (typical)= 0.001 m^2
(size and location may vary depending
on sample holder in use)

Sample Clamping Plate

Test Sample

Sample Clamping Plate

Duct Width = 0.025 m
Duct Height = 0.0025 m or 0.0050 m
(two different cells available)
Duct Length = 0.13 m

Flow Inlet
or Outlet

Lower Half of Flow Cell

Figure 3. Schematic and Dimensions of the Sample Holder for the DMPC.

The sample sizes are kept quite small to make it possible to evaluate novel membranes and laminates, which are often produced in quantities too small for testing by some of the standard water vapor diffusion test methods. The small sample area makes it necessary to test at different locations across a typical roll of fabric to adequately characterize a given material. Sample mounting methods vary according to the material being tested. Thin materials, such a laminated materials and woven cloth, were originally tested with rubber sealing gaskets to prevent leakage, but the sealing proved to be unnecessary for most materials; the clamping force provided by the mounting bolts has proven to be sufficient to prevent any leakage. Thick materials which are highly permeable require special sealing methods such as edge sealing by molten wax, or the use of a curable sealant. The testing of thicker materials also requires a larger sample area to minimize factors such as edge effects.

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Diffusion Test Procedure

The actual test is conducted under the control of a personal computer (PC) connected to the flow controllers, automated valves, and the various measurement transducers through input and output boards (see Figure 2). Various options exist within the software for operator input setpoint information, or preset files containing the setpoint information. The computer applies the proper setpoint voltage to each controller to produce the desired relative humidity in the upper and lower gas streams entering the DMPC. The A/D board in the PC reads analog voltage outputs of the relative humidity, RTD, thermocouples, differential pressure transducer, mass flow meters, etc., records the data on disk, calculates parameters of interest, and plots results to the PC screen. The software applies operator-determined equilibration criteria to determine when equilibration has been reached for that setpoint. Once equilibration is reached, the results (humidity, calculated flux, etc.) may be output to a printer and to a data file on disk. The computer then proceeds to the next setpoint and repeats the process.

The pressure drop across the sample is monitored by means of an MKS Baratron Type 398 differential pressure transducer, with a Type 270B signal conditioner (MKS Instruments, Inc.). For measurement of pure diffusion, especially for materials such as fabrics, which may be quite permeable to convective flows, it is important to make sure that the pressure drop across the sample is zero, so that transport takes place only by pure diffusion. The pressure drop is continuously monitored and displayed, and is controlled by means of two automated valves at the outlets of the cell. For the permeable fabrics, this system also allows one to do testing under controlled conditions of a defined pressure drop across the sample, so that transport takes place by both diffusion and convection. This makes it possible to determine an air permeability value from the apparatus, in addition to the water vapor diffusion properties of the test sample [15].

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A total resistance to mass transfer is defined as the simple addition of an intrinsic diffusion resistance due to the sample (R_i) and the diffusion resistance of the boundary air layers (R_{bl}):

$$\frac{\dot{m}}{A} = \frac{\Delta \overline{C}}{\left(R_i + R_{bl} \right)}$$ (3)

$$R_i = \left[\frac{\Delta \overline{C}}{\left(\frac{\dot{m}}{A} \right)} \right] - R_{bl}$$ (4)

$\dot{m}$ = mass flux of water vapor across the sample (kg/s)
A = area of test sample (m²)

$\Delta \overline{C}$ = log mean concentration difference between top and bottom nitrogen streams (kg/m³)
R_i = intrinsic diffusion resistance of sample (s/m)
R_{bl} = diffusion resistance of boundary air layers (s/m)

The log mean concentration difference across the sample is appropriate since there is a significant change in the concentration of the gas stream both below and above the sample. In addition, the gas streams may not necessarily be in parallel unidirectional (cocurrent) flow, but may be run in counter flow to maintain a more constant concentration gradient across the sample. The log mean concentration difference [16] is defined as:

$$\Delta \overline{C} = \frac{\Delta C_a - \Delta C_b}{\ln \left(\Delta C_a / \Delta C_b \right)}$$ (5)

ΔC_a = concentration difference between the two gas streams at one end of the flow cell (kg/m³)

ΔC_b = concentration difference between the two gas streams at the other end of the flow cell (kg/m³)

For parallel cocurrent flow, the concentration differences are between the top and bottom incoming flow at one end of the cell (ΔC_a), and the difference between the top and bottom outgoing flows at the other end of the cell (ΔC_b). For countercurrent flow, the concentration differences are between the incoming and outgoing flows at one end of the cell (ΔC_a), and the incoming and outgoing flows at the other end of the cell (ΔC_b).

Example of Concentration-Dependent Diffusion in Membrane Laminates

Vapor transport across nonporous hygroscopic polymer membranes and films is often affected by the amount of water present in the polymer. The DMPC, when operated in the pure vapor diffusion mode (no pressure drop across the sample) is capable of showing this concentration-dependent transport behavior [7-10].

An example is shown for materials tested in a separate study [9]. One of the materials was a porous nonhygroscopic membrane, and the other two contained hydrophilic polymer films. The test temperature was 20°C and nominal gas flow rate was 2000 cm³/min. The sequence of test setpoints begin at low mean relative humidity and worked systematically up to high mean humidities, so that the hydrophilic samples were progressively absorbing more water vapor. A constant humidity gradient of 0.50 (50% r.h.) was maintained across all the samples to allow direct comparison of water vapor fluxes for the different setpoints. Table 1 presents the sequence of setpoints used for each sample.

Table 1. Typical Humidity Test Setpoints (at 20°C)

Setpoint #	Input Relative Humidity on Top	Input Relative Humidity on Bottom	Mean Relative Humidity
1	0.5	0.0	0.25
2	0.6	0.1	0.35
3	0.7	0.2	0.45
4	0.8	0.3	0.55
5	0.9	0.4	0.65
6	1.0	0.5	0.75

Water vapor transport results are shown in terms of the "mean relative humidity", which is simply the average of the humidity on the two sides of the sample. The analogy is to the water vapor sorption isotherm, which is the equilibrium water content of a hygroscopic polymer as a function of relative humidity. The mean relative humidity has proven to be useful in showing the mass transport behavior in terms of concentration dependence of the permeability coefficient [4,7,8].

Figure 4 shows the measured water vapor diffusion resistance of the three materials using the setpoints of Table 1. The diffusion resistance given in Figure 4 is the sum of the intrinsic material resistance (R_i) plus the boundary layer resistance (R_{bl}), as defined in equation (4). In this report we present the combined resistances as a single value, but procedures exist for separately determining the intrinsic material mass transfer and boundary layer resistances [7,8]. The results show the expected increase in water transport with humidity for the two materials (B and C) with a hygroscopic polymer component. In Material "A", water vapor transport takes place in the gas-filled pore structure of the material. Porous textiles generally show no dependence of water vapor diffusion resistance on "mean relative humidity" since the water vapor is simply diffusing through pore spaces, and does not go through the sequence of absorbing into, diffusing through, and desorbing from the other side of a polymeric layer.
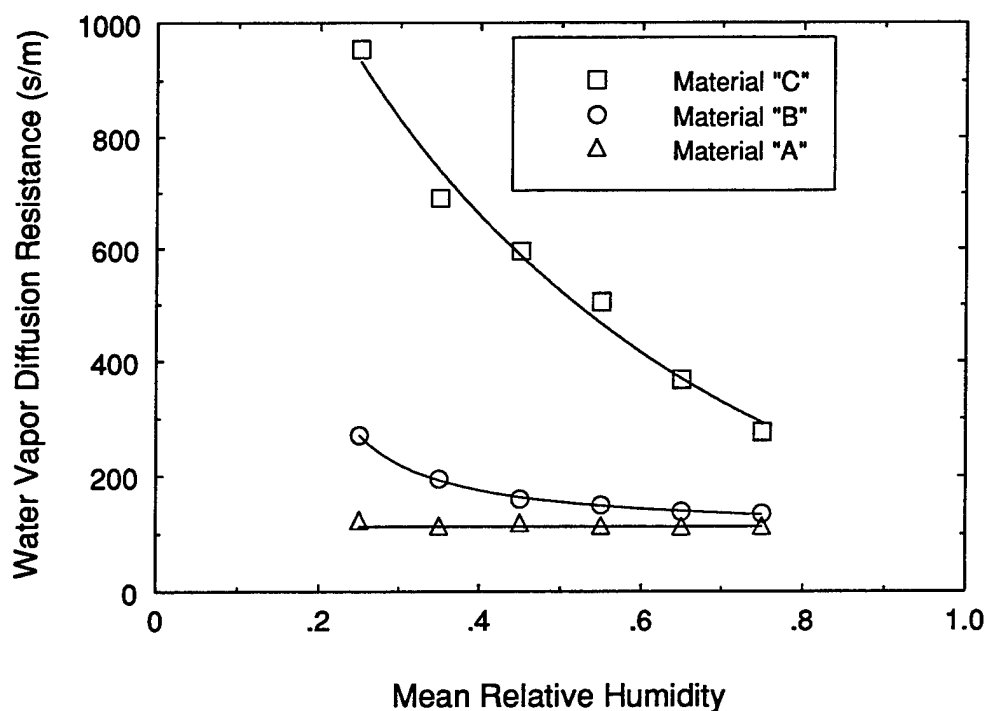

Figure 4. Water Vapor Diffusion Resistance Determined by DMPC.

Figure 5 shows the water vapor fluxes across the three samples, again in terms of the "mean relative humidity." Material "A", the porous nonhygroscopic membrane, shows no concentration dependence, while the other two materials with hygroscopic polymer layers show much greater water vapor transport under conditions of high water content in the polymer layer.
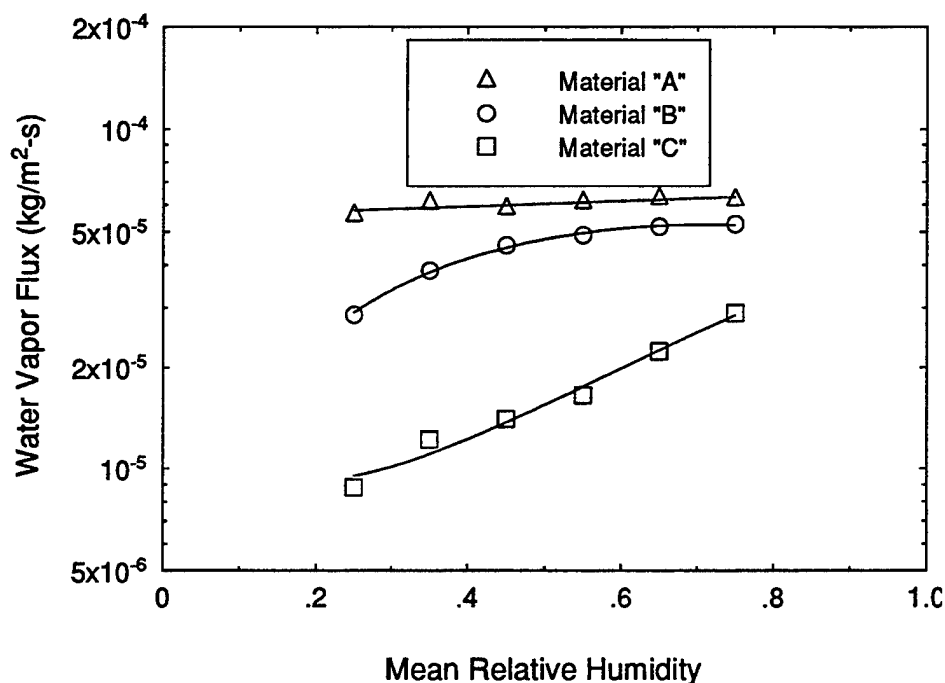

Figure 5. Water Vapor Flux Under a Constant Humidity/Concentration Gradient.

The ability to systematically vary test conditions to show this kind of behavior is the primary advantage of using the DMPC over other textile test methods, which usually prescribe a single temperature and relative humidity. The ability to bracket the possible range of intrinsic transport properties under various environments makes it less likely that a single set of test conditions will give misleading results during a material evaluation/selection process.

3. Results

Test Conditions

The setpoints used for each material are summarized in Table 2. The first six setpoints are at a constant humidity gradient of 0.50 (50%). The final setpoint is at the maximum humidity gradient of 1.0 (100%). This final setpoint is the one used to show the temperature dependence of the water vapor transport properties. Some of the samples tested proved to have very low water vapor fluxes at the low temperatures, so it was necessary to maximize the possible water vapor flux by providing the largest possible concentration difference across the sample.

Table 2. Summary of Test Conditions and Setpoints

Test Temperatures (°C) -- 3, 10, 20, 30, 40 ; Flow Rate -- 500 cm³/min

Setpoint #	Input Relative Humidity on Top	Input Relative Humidity on Bottom	Mean Relative Humidity
1	0.50	0.00	0.25
2	0.60	0.10	0.35
3	0.70	0.20	0.45
4	0.80	0.30	0.55
5	0.90	0.40	0.65
6	1.00	0.50	0.75
7	1.00	0.00	0.50

The individual test results for each material are plotted in Appendix A, and the results are given in table form in Appendix B.

Concentration-Dependent Water Vapor Diffusion

Figure 6 shows the water vapor diffusion resistance of the nine materials over a range of mean relative humidities (obtained using setpoints 1-6 of Table 2), at the single temperature of 20°C. Setpoint 7 is omitted from these plots for clarity. Figure 6 has not had the effective boundary layer resistance subtracted off from the values. The boundary layer resistance for each temperature condition is given in Appendix B. The Polyester/Polyether Membrane, PTFE/PAO/PU Membrane, and PTFE/PAO/PU Laminate all have nearly identical properties, and are superimposed on each other in Figure 6.
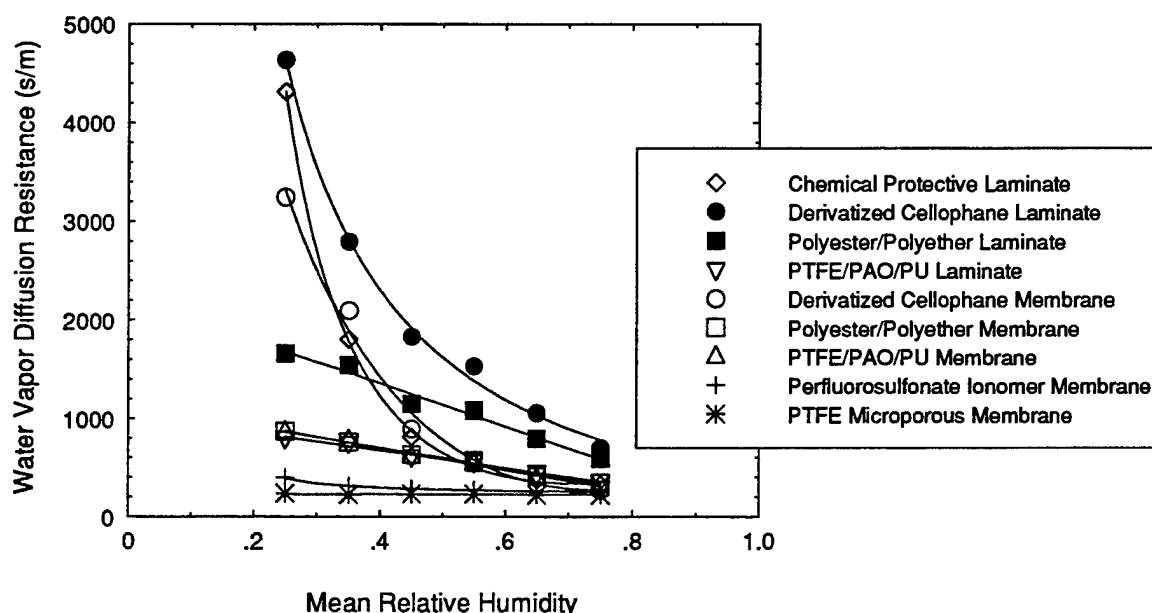

Figure 6. Water Vapor Diffusion Resistance as Function of "Mean Relative Humidity."

Figure 6 indicates that most of the membranes and laminates are greatly influenced by the relative humidity test conditions. In particular, the two laminates containing the polyester/polyether copolymer membrane and the derivatized cellophane membrane show drastic changes. In dry environmental test conditions, both materials have poor water vapor transport properties, but at higher humidities, they both become superior to most of the other materials tested. At the higher relative humidities, the hydrophilic membranes contain more sorbed water, and there is much less resistance to the diffusion of water molecules through the polymer matrix. It is clear that standard test methods which use a single set of humidity conditions could misrepresent the relative transport behavior of this group of materials.

Intrinsic Resistances

The resistances given in Figure 6 include the boundary layer resistance due to the air flow over the surface of the sample, as defined by Equation (4). The boundary layer resistance at a given temperature may be found from the microporous PTFE sample, which has been found to have an intrinsic diffusion resistance of approximately 7 s/m at 20°C [7,8]. The boundary layer resistance may be found by subtracting the intrinsic resistance of the PTFE membrane (R_i) from the total measured resistance, after correcting for the temperature dependence of the diffusion coefficient of water vapor in air (D_{air}):

$$R_i(T) = R_i(20°C)[D_{air}(20°)/D_{air}(T)] \tag{6}$$

where the temperature-dependent diffusion coeffient D_{air} (m²/s) is given by:

$$D_{air}(T) = (2.23 \times 10^{-5})[(T+273.15)/273.15]^{1.75} \tag{7}$$

The boundary layer resistance as a function of temperature (averaged over all the "mean relative humidity" conditions) is shown in Figure 7. Also shown in Figure 7 is the boundary layer resistance which has been normalized by the factor $[D_{air}(20°)/D_{air}(T)]$ from equation (6).
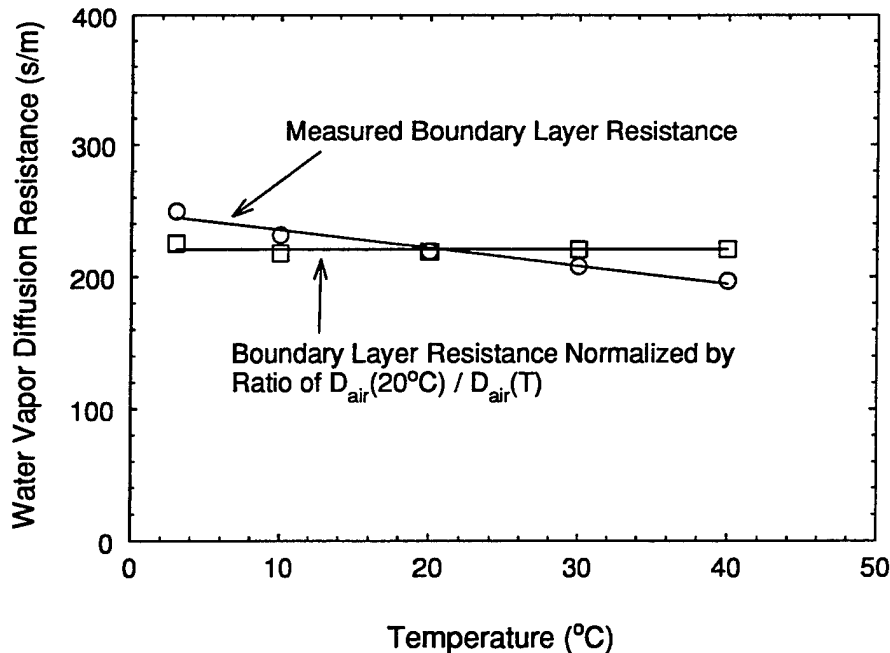

Figure 7. Variation in Boundary Layer Resistance due to Temperature Dependence of Diffusion Coefficient of Water Vapor in Air.

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The boundary layer resistance (normalized for temperature) may be subtracted from the total measured resistance to give the intrinsic diffusion resistance of each material, as shown in Figure 8. The intrinsic resistance is a property which compares well between different test methods, which may all differ in the air flow conditions over the test sample [7,8]. Boundary layer resistances and total water vapor diffusion resistance for each material and test condition are listed in Appendix B. Figure 8 is nearly identical to Figure 6, since the subtraction of the boundary layer resistance has simply shifted the curves downward by the amount of the measured boundary layer resistances.
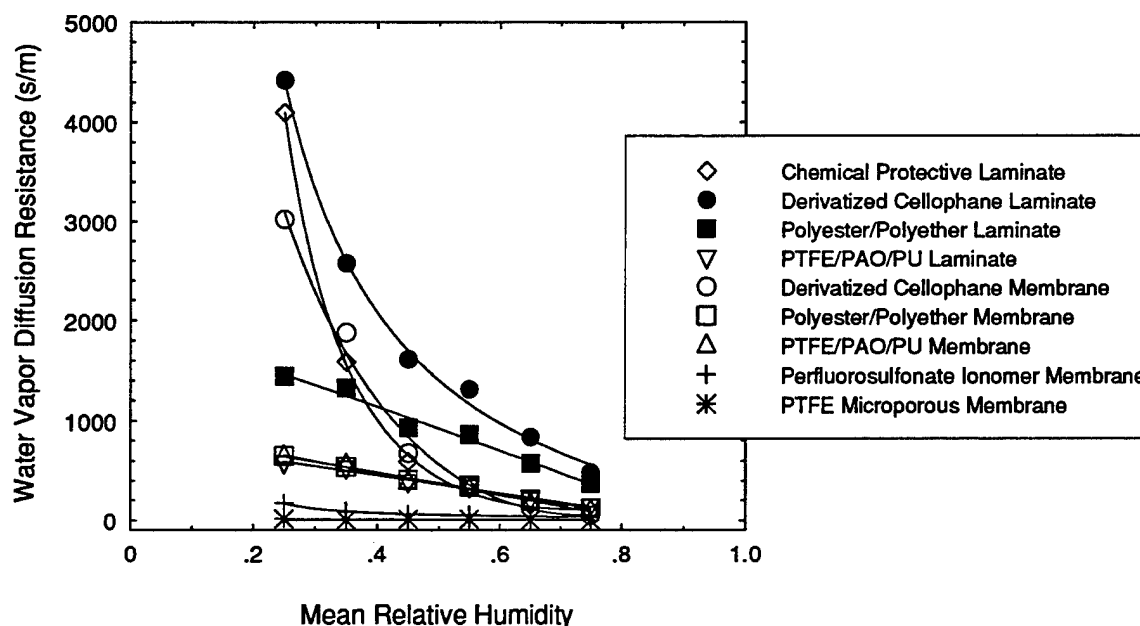

Figure 8. Intrinsic Diffusion Resistance at Conditions of 20°C, after Subtraction of Boundary Layer Resistance.

Temperature-Dependent Water Vapor Diffusion

Figure 9 shows the water vapor flux of the nine materials as a function of temperature for the single relative humidity condition of 1.0 (100%) and 0.0 (0%) on the two sides of the sample (setpoint #7 of Table 2). This corresponds to a "mean relative humidity" of 0.50.
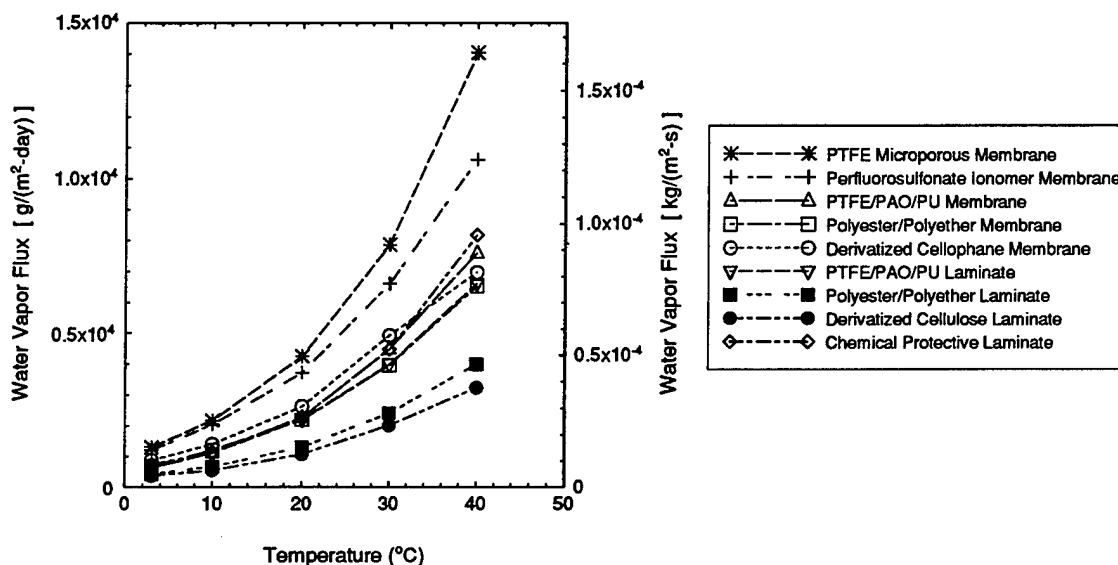

Figure 9. Water Vapor Flux as Function of Temperature.

Figure 9 shows the measured water vapor flux across each test sample increasing in an exponential fashion with temperature. There are some slight differences in relative fluxes at each temperature, but for the most part, the relative ranking of each material is maintained across all the temperature conditions.

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Figure 10 shows the same information plotted in an Arrhenius fashion, where the flux is a function of the reciprocal temperature. Figure 10 helps to show that the water vapor flux for each material scales with temperature in the same way. The most important factor in the shape of the curves in Figures 9 and 10 doesn't have anything to do with the properties of the material, but simply reflects the relationship between the saturation vapor pressure of water and temperature.
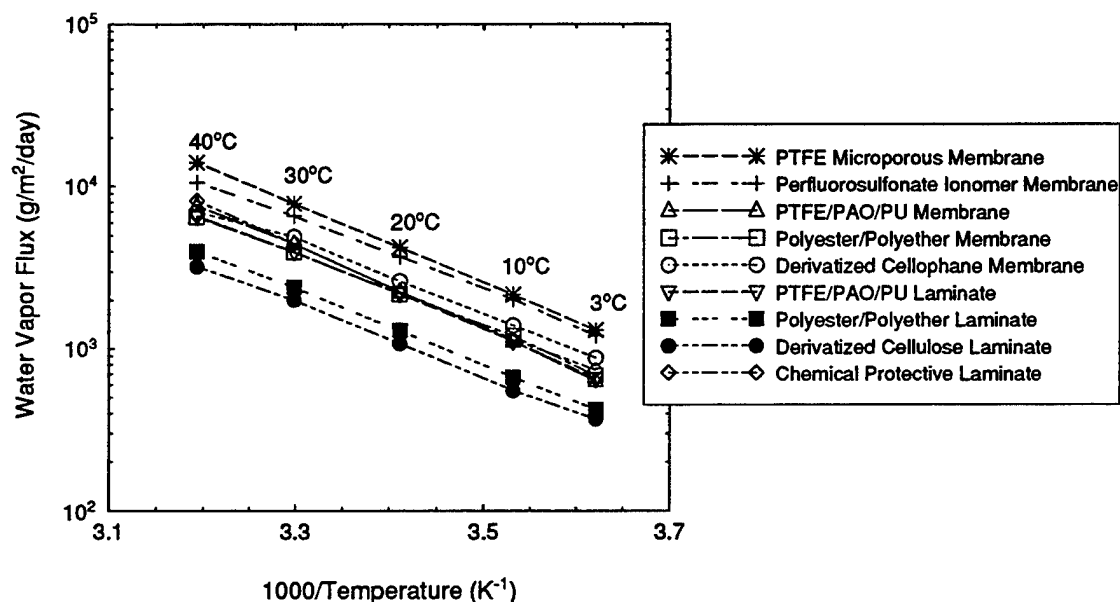

Figure 10. Water Vapor Flux as Function of Reciprocal Temperature.

It is a fairly common practice to use plots similar to Figure 10 to derive an Arrenhius constant from the slope of the curves to derive a temperature-dependent material transport property. However, flux measurements by themselves can be very misleading, since they are not normalized with respect to the gradient across the membrane, and are often greatly influenced by additional resistance factors due to the boundary layers formed by gas flow conditions over the surface of the test sample.

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Figure 11 shows the measured water vapor diffusion resistance as a function of temperature, over the range of 3-40°C, for relative humidity conditions of 1.0 (100%) and 0.0 (0%) on the two sides of the sample (setpoint #7 of Table 2).
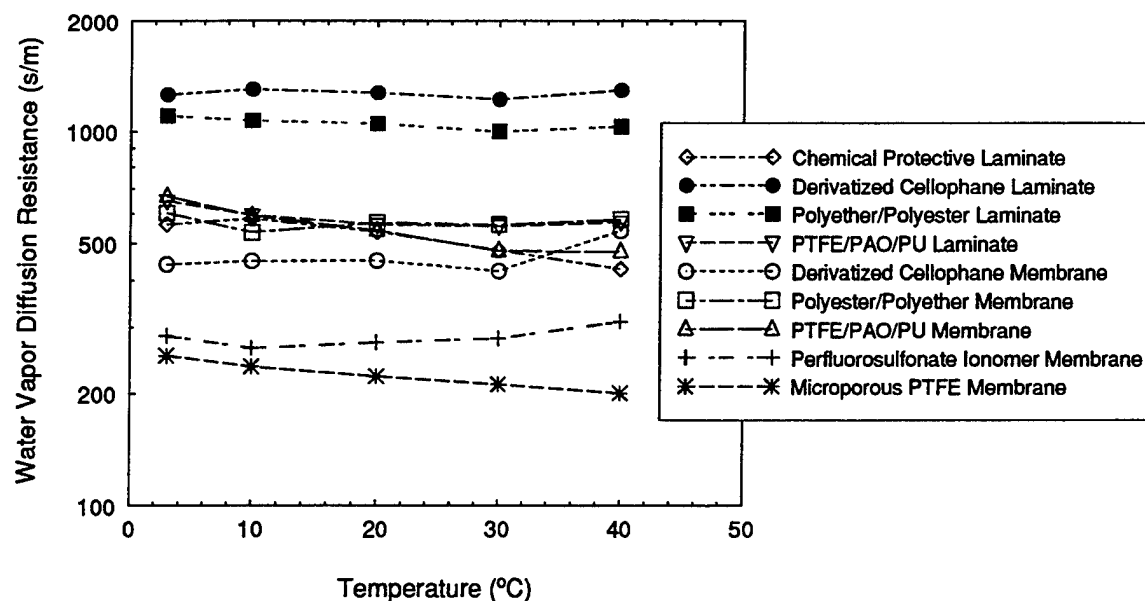

Figure 11. Water Vapor Resistance as Function of Temperature.

Since Figure 11 is given in terms of resistance, the variation of saturation vapor pressure as a function of temperature no longer influences the relative ranking of each material. As described previously, additional corrections may be made for the presence of boundary layer resistances due to the test system, and the temperature dependence of the diffusion coefficient of water vapor in air.

Figure 11 shows diffusion properties vary little with temperature, as compared to the property variation due to relative humidity test conditions. There are no dramatic changes in ranking due to temperature as there were in the ranking conducted over a range of relative humidity conditions. In general, the measured diffusion resistance is expected to decrease at higher temperatures [17]. However, Figure 11 shows that there are several instances where no discernible change in properties is seen. In one instance (the perfluorosulfonate ionomer membrane) the diffusion resistance increases with temperature, which has been observed occasionally for materials such as silicone rubber, nylon, and polyvinyl alcohol [18]. As discussed previously, the observed decrease in diffusion resistance of the microporous PTFE membrane is due to the temperature dependence of the diffusion coefficient of water vapor in air.

Figure 11 showed minimal temperature effects for a single relative humidity test condition. Other relative humidity test conditions showed a similar lack of drastic influence of temperature on measured diffusion resistance. This is illustrated in Figure 12 using a hygroscopic monolithic membrane and a microporous nonhygroscopic membrane.
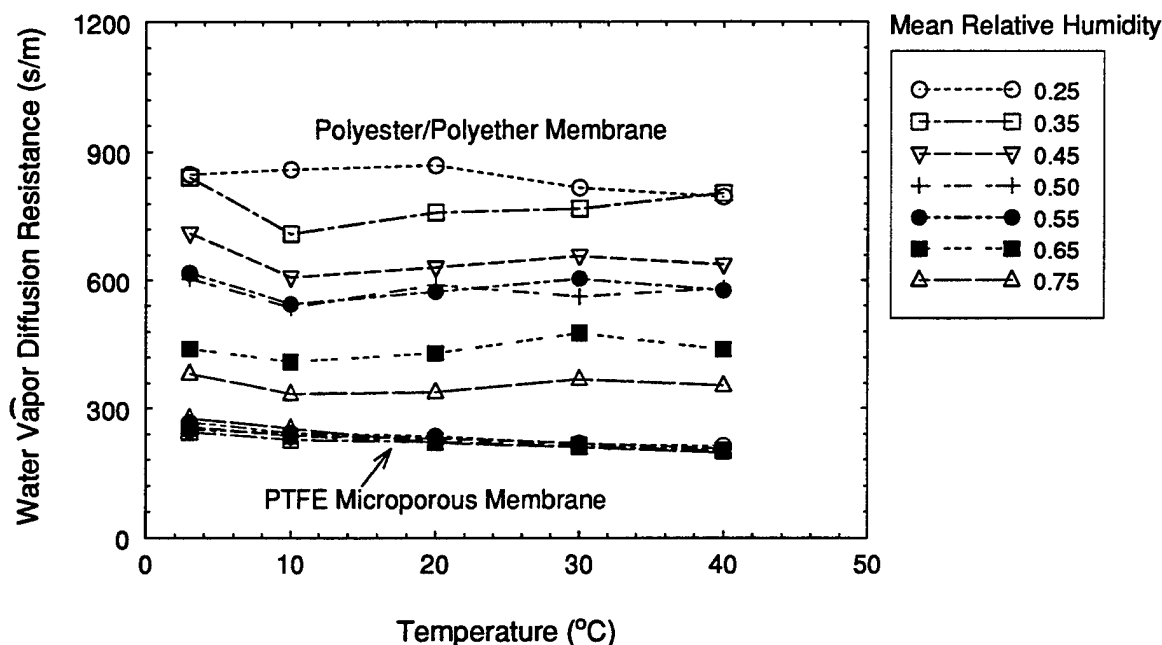

Figure 12. Effect of Temperature on Diffusion Resistance for a Hygroscopic and Nonhygroscopic Membrane, at Various Humidity Conditions.

Test results for the porous PTFE membrane superimpose on each other for the various mean humidity test conditions, reflecting the basic mechanism of vapor diffusion through gas-filled pore spaces. The polyester/polyether membrane shows a very pronounced difference at different mean humidity levels (polymer water content), yet for a given mean relative humidity the diffusion resistance remains fairly constant over the range of temperatures used.

Figure 13 shows the same data as Figure 12, except that the resistance is now plotted as a function of mean relative humidity. It is clear that the hygroscopic membrane is much more sensitive to polymer water content (related to mean relative humidity) than the test temperature used. This is probably due to the fact that the water vapor sorption isotherm in hygroscopic polymers is relatively constant over this temperature range [19].
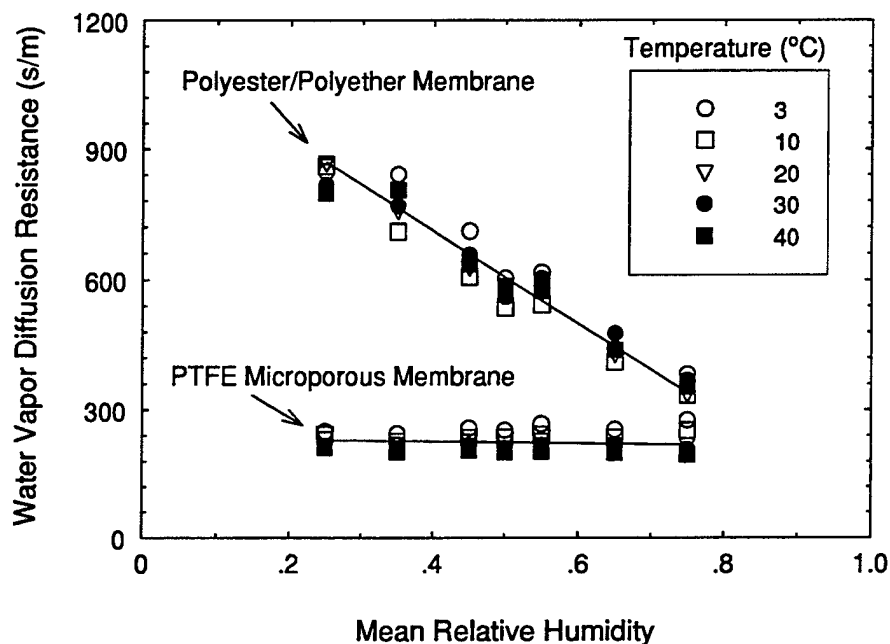

Figure 13. Effect of Humidity Conditions on Diffusion Resistance for a Hygroscopic and Nonhygroscopic Membrane, at Various Temperatures.

For the nine materials evaluated in this study, vapor transport property variations due to changes in polymer water content are much more significant than changes due to temperature. This is emphasized in Figure 14, which shows the measured variation in diffusion resistance due to these two different factors.
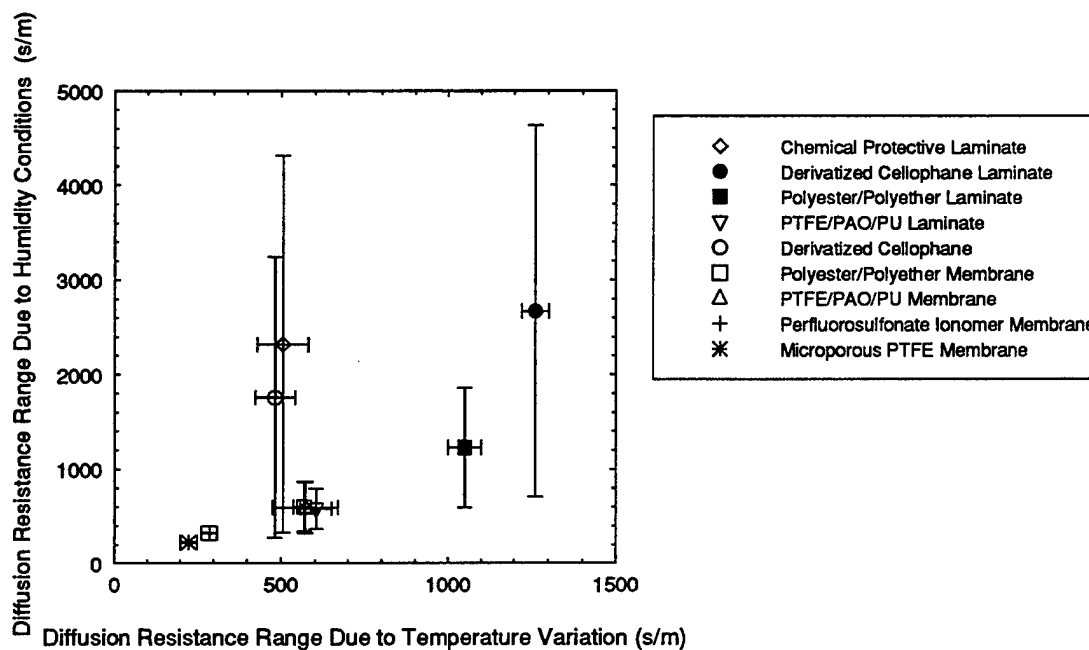

Figure 14. Range of Variation in Water Vapor Resistance Values due to Temperature and "Mean Relative Humidity."

4. Conclusions

The Dynamic Moisture Permeation Cell (DMPC) was used to evaluate the temperature-dependent water vapor transport behavior of nine polymer membranes and membrane/textile laminates. The DMPC's control over vapor concentration, gas flow rate, and temperature allowed concentration-dependent effects to be distinguished from temperature-dependent effects.

Measured changes in water vapor flux over the temperature range of 3°C to 40°C were primarily due to the fundamental physical relationship between temperature and the saturation vapor pressure of water -- not to intrinsic changes in polymer permeability. The transport property of water vapor diffusion resistance, where flux is normalized by the water vapor concentration gradient, is shown to be more suitable than flux measurements for comparing the transport behavior of different materials. The observed temperature dependence of water vapor transport through the interconnected gas-filled passages of a microporous membrane was accounted for by the known temperature dependence of the diffusion coefficient of water vapor in air.

The potential range of tested property variations was shown to be much more influenced by polymer water content (concentration dependence) than by any temperature effects for the nine materials used in this study. As long as a fundamental property such as resistance is used to evaluate materials, it seems unlikely that moderate differences in temperature would affect the results of comparative screening efforts to rate the performance of polymer membranes or textile laminates.

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Appendix A.

Individual Plots of Water Vapor Resistance Results

Individual plots are shown for water vapor resistance versus temperature, for each relative humidity condition. The same information is shown in two different ways: 1) using temperature as the x-axis, and 2) using "mean relative humidity" as the x-axis.
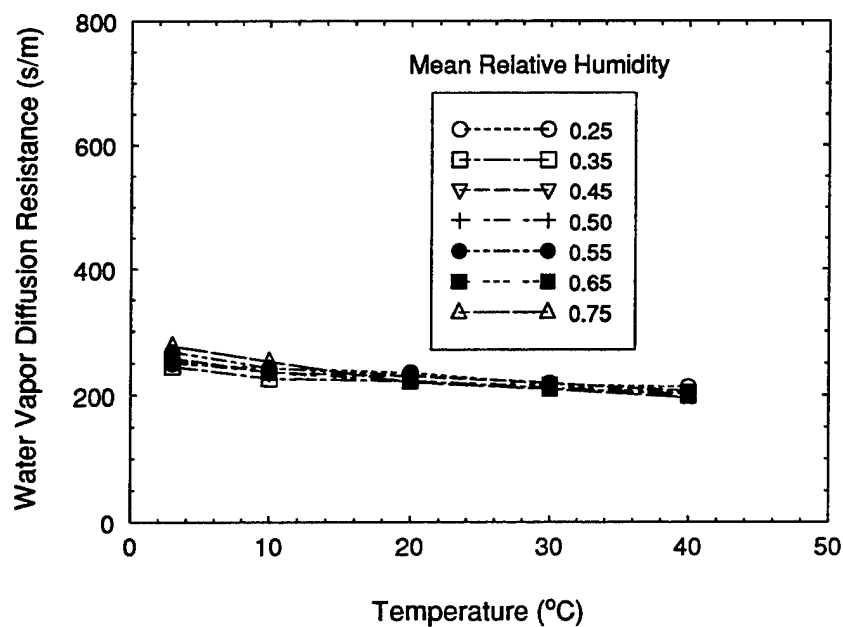

Figure A-1. Effect of Temperature on Water Vapor Diffusion Resistance of Microporous PTFE Membrane.
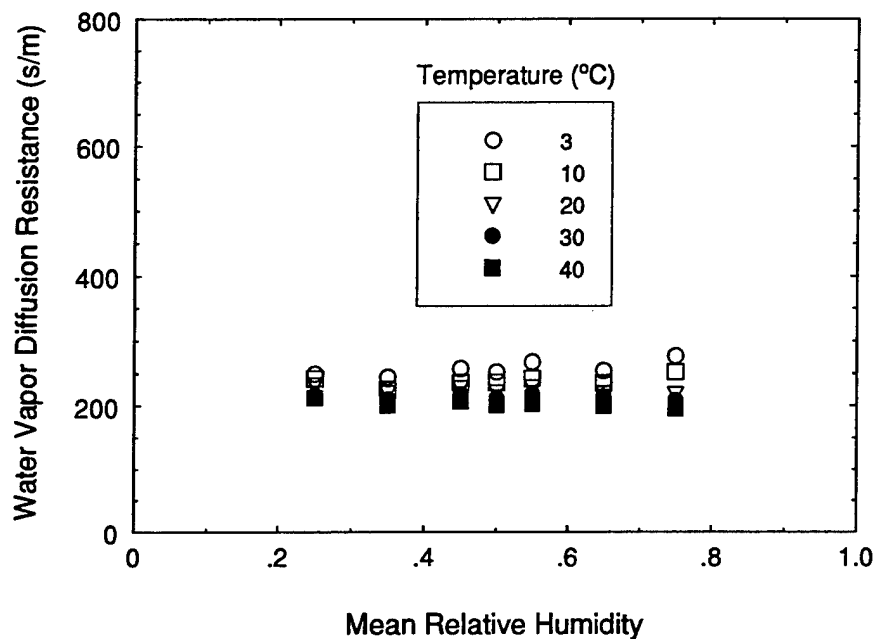

Figure A-2. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of Microporous PTFE Membrane.
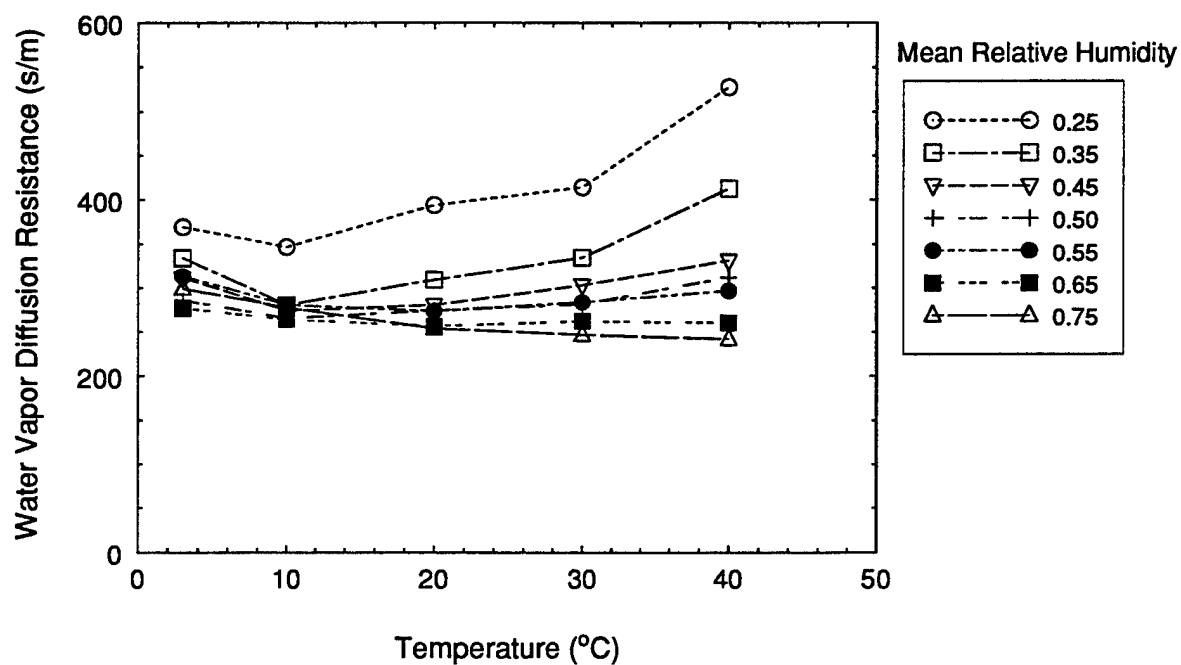
28

Figure A-3. Effect of Temperature on Water Vapor Diffusion Resistance of Perfluorosulfonate Ionomer Membrane.
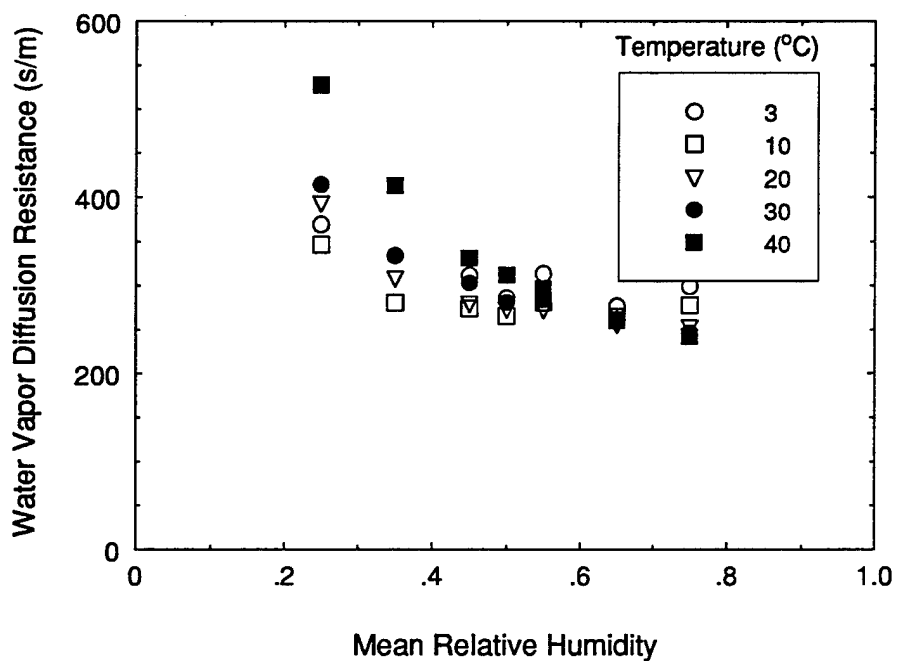

Figure A-4. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of Perfluorosulfonate Ionomer Membrane.
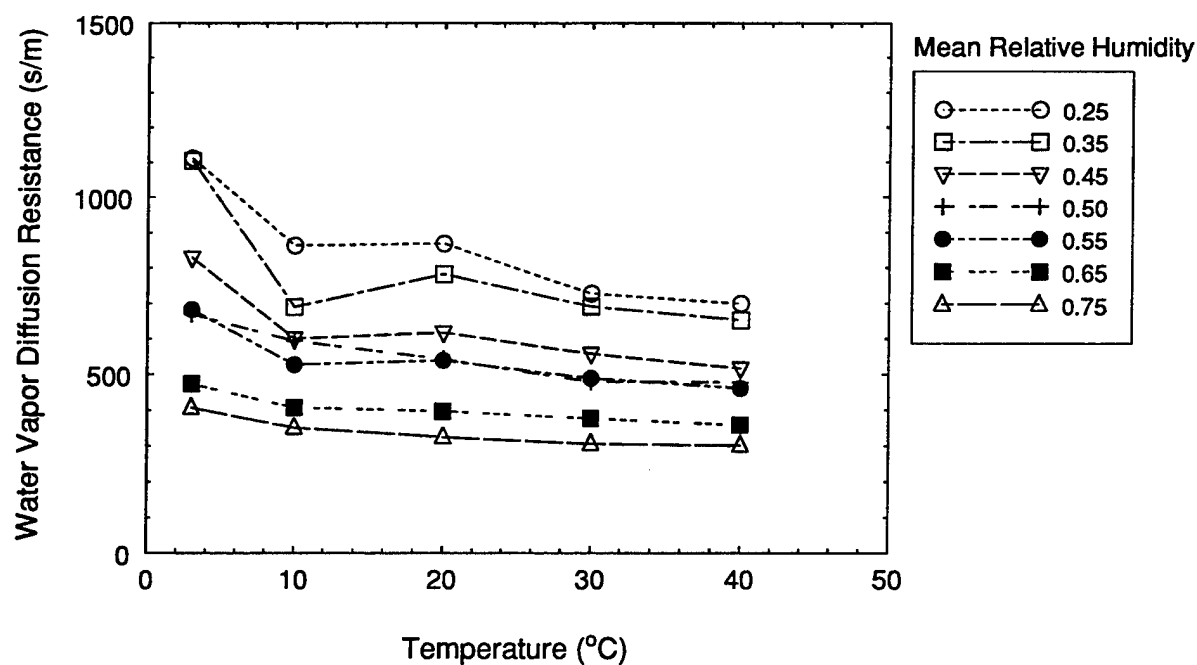
29

Figure A-5. Effect of Temperature on Water Vapor Diffusion Resistance of PTFE/PAO/ PU Membrane.
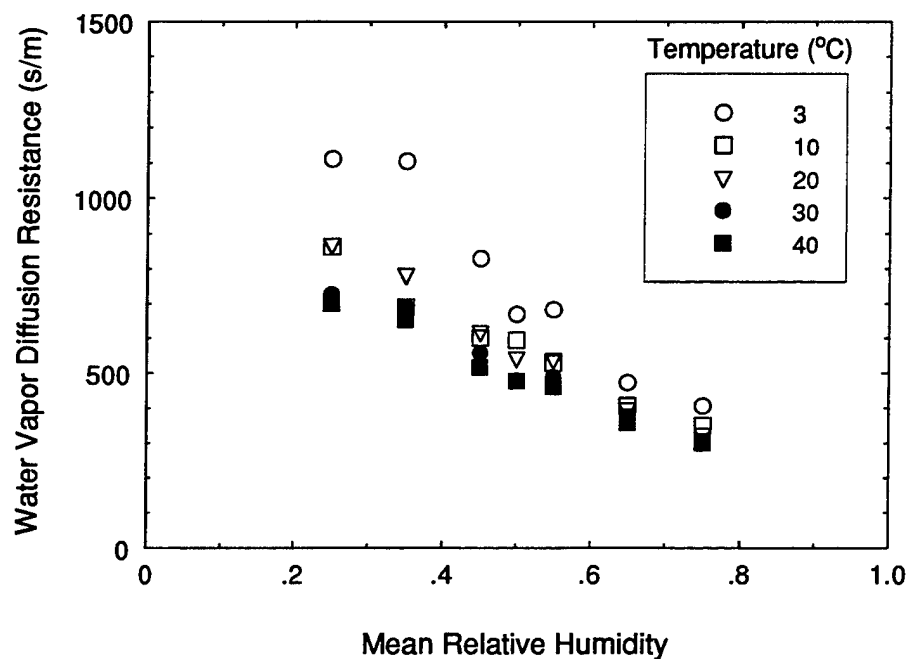

Figure A-6. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of PTFE/PAO/PU Membrane.
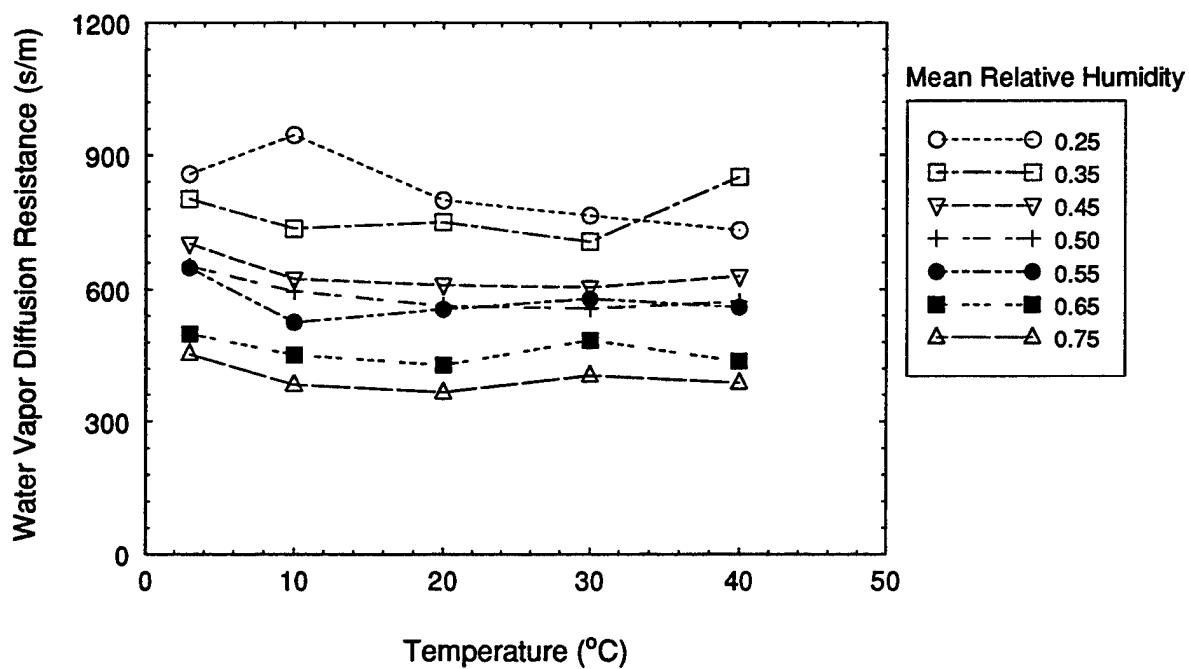
30

Figure A-7. Effect of Temperature on Water Vapor Diffusion Resistance of PTFE/PAO/ PU Laminate.
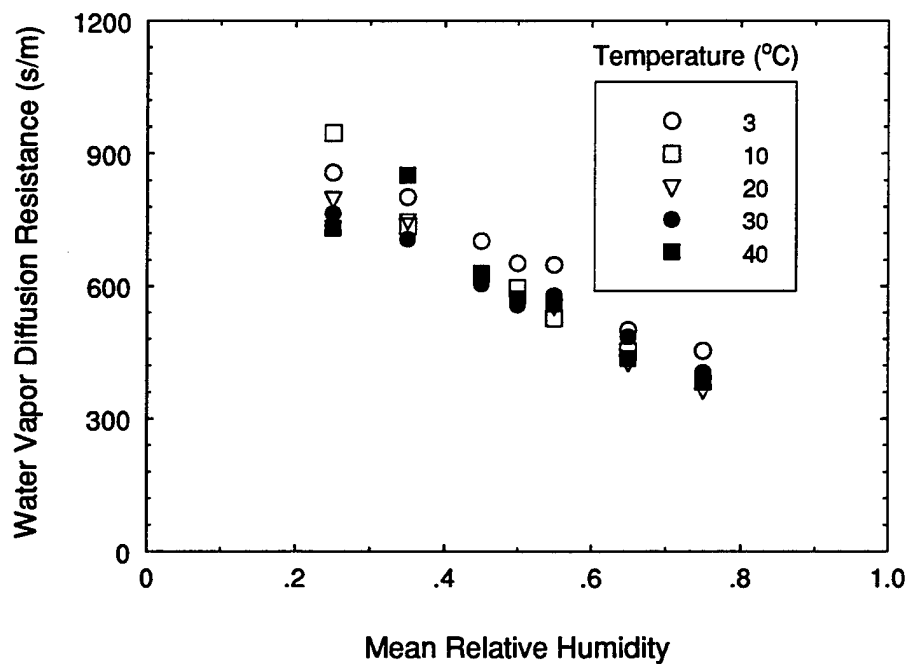

Figure A-8. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of PTFE/PAO/PU Laminate.

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Figure A-9. Effect of Temperature on Water Vapor Diffusion Resistance of Polyester/ Polyether Membrane.

Figure A-10. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of Polyester/Polyether Membrane.
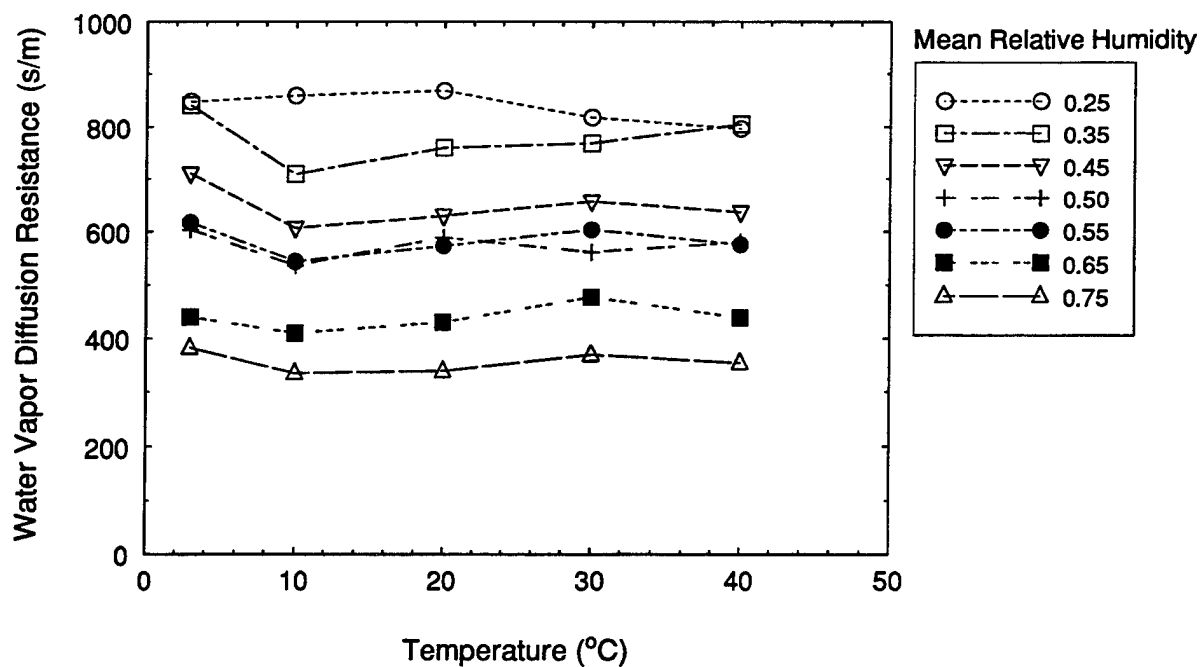
32

Figure A-11. Effect of Temperature on Water Vapor Diffusion Resistance of Polyester/ Polyether Laminate.
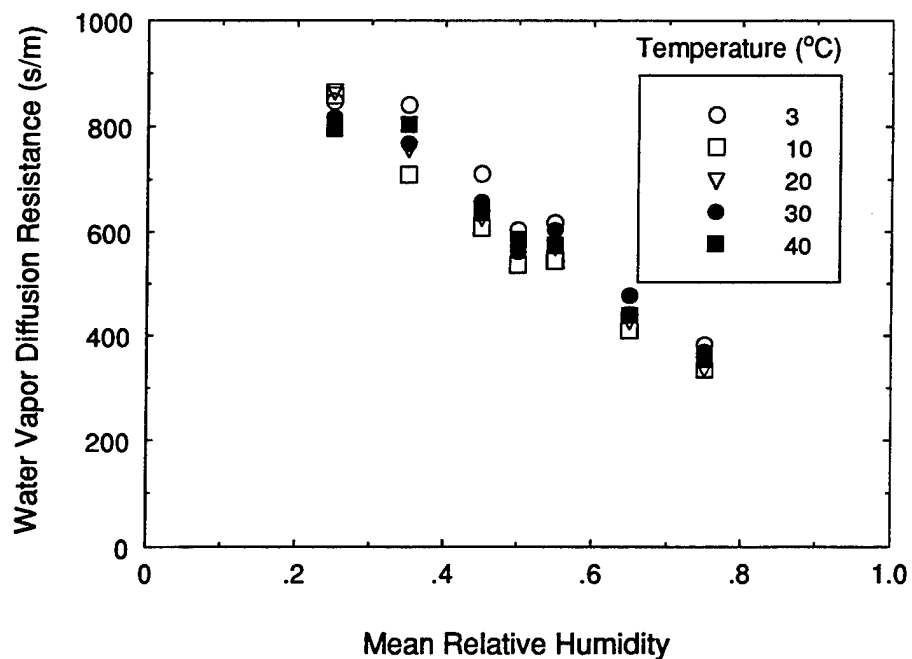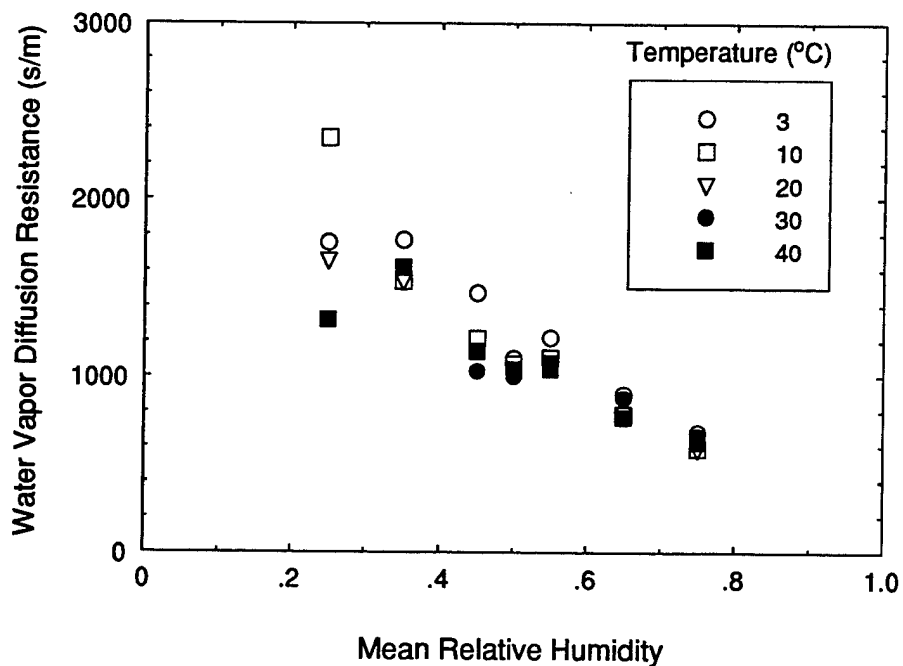

Figure A-12. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of Polyester/Polyether Laminate.

Figure A-13. Effect of Temperature on Water Vapor Diffusion Resistance of Derivatized Cellophane Membrane.

Figure A-14. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of Derivatized Cellophane Membrane.

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Figure A-15. Effect of Temperature on Water Vapor Diffusion Resistance of Derivatized Cellophane Laminate.

Figure A-16. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of Derivatized Cellophane Laminate.
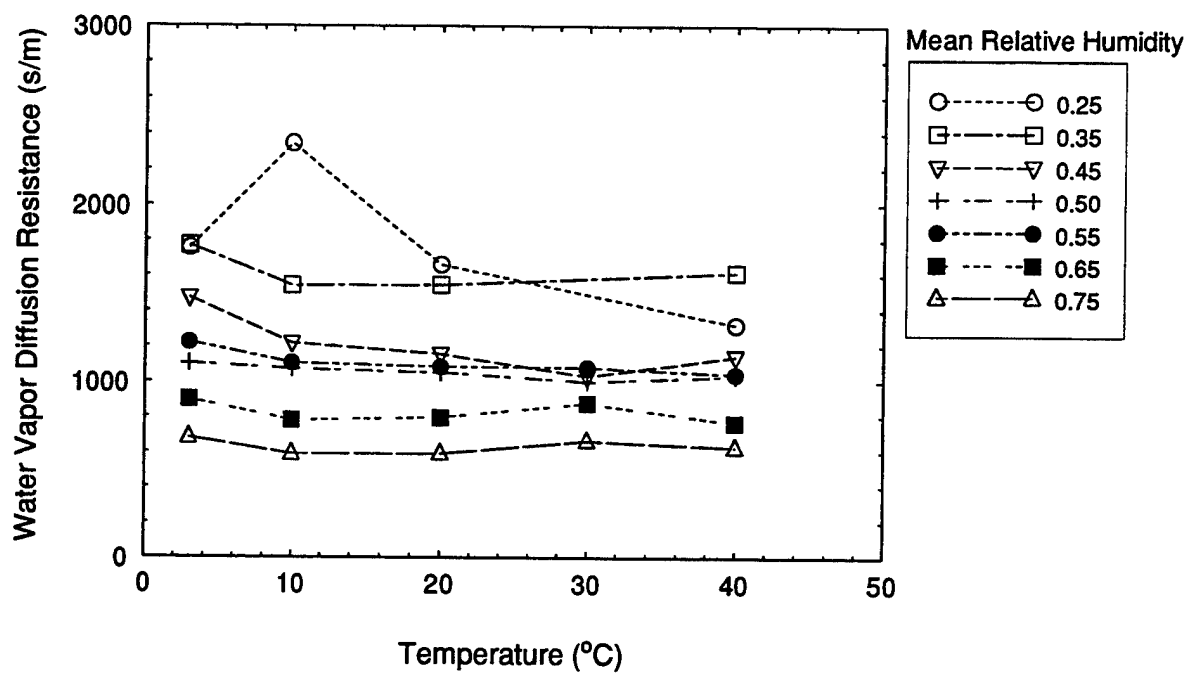
Figure A-17. Effect of Temperature on Water Vapor Diffusion Resistance of Chemical Protective Laminate.

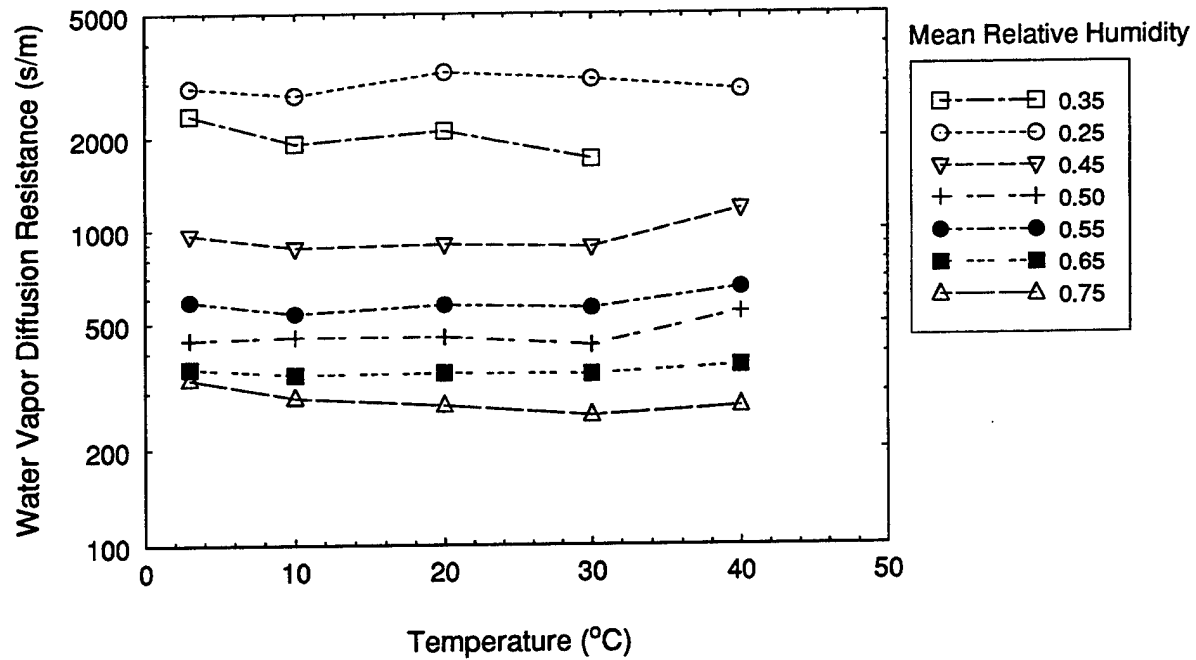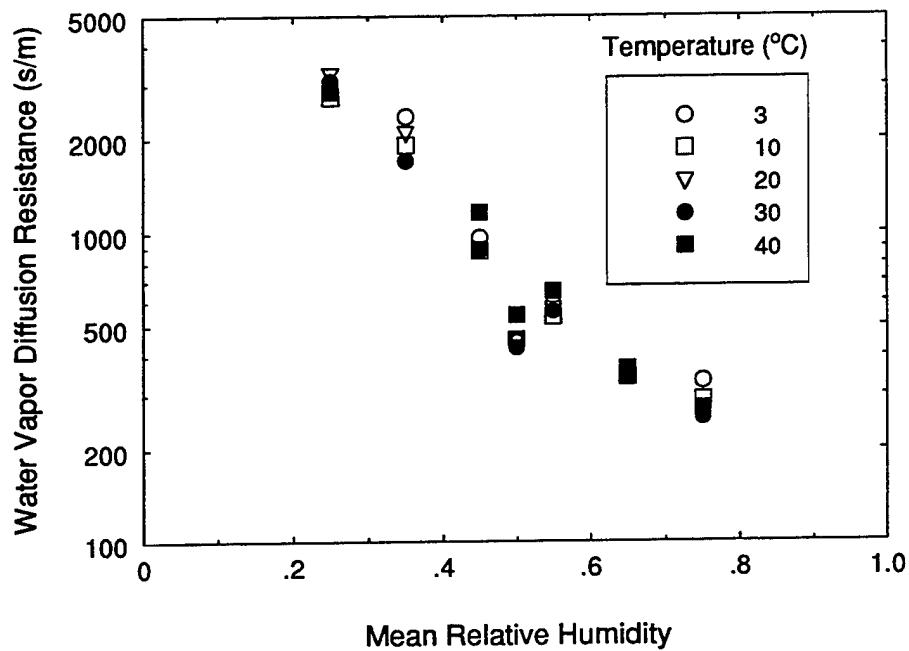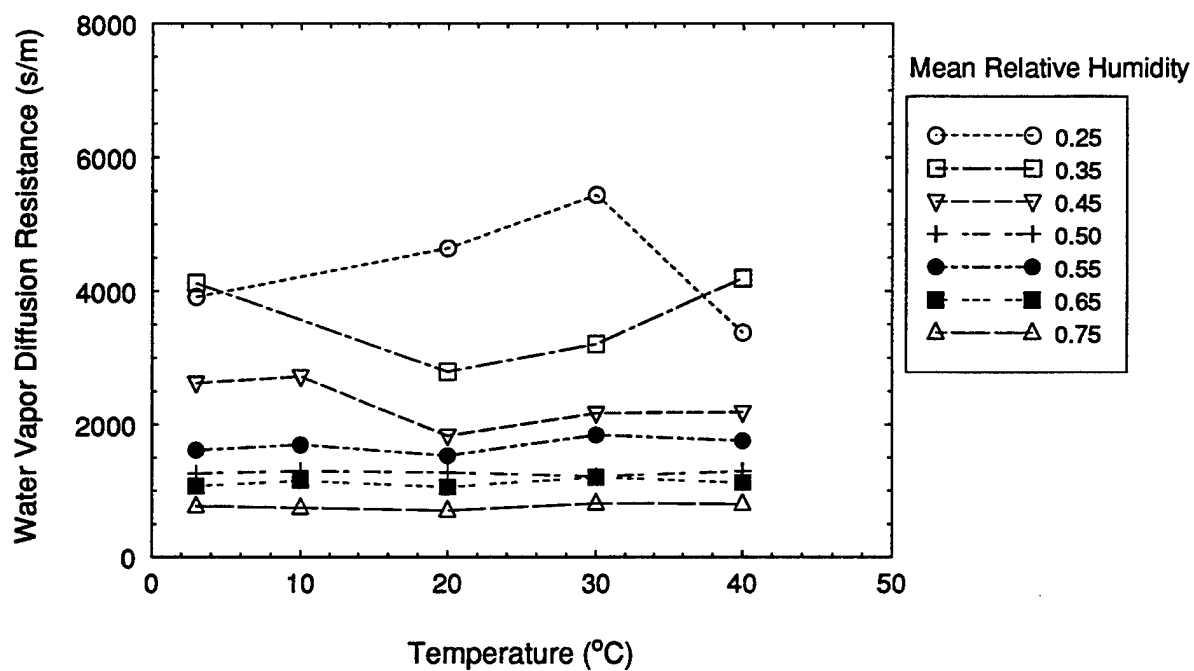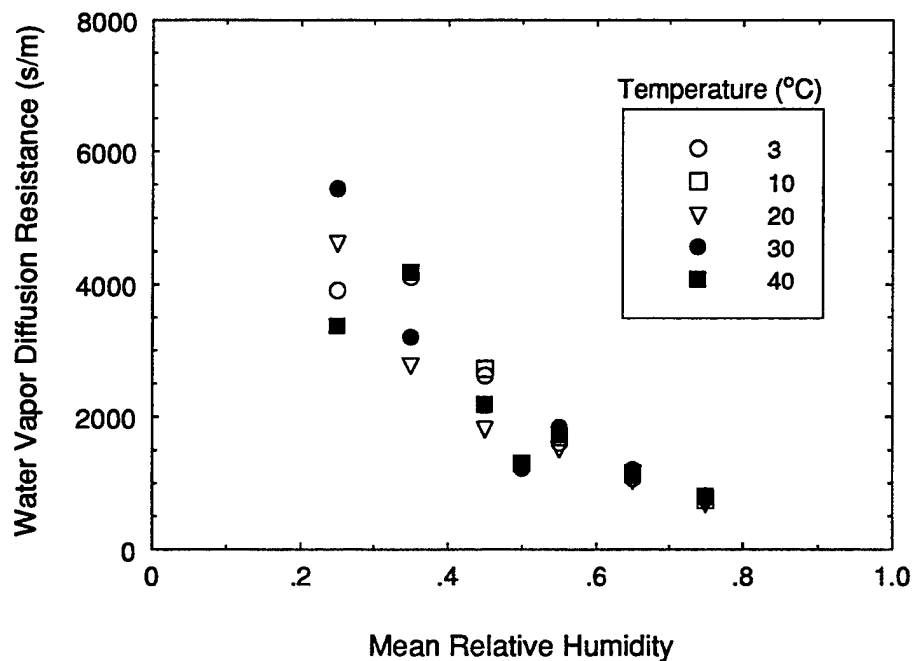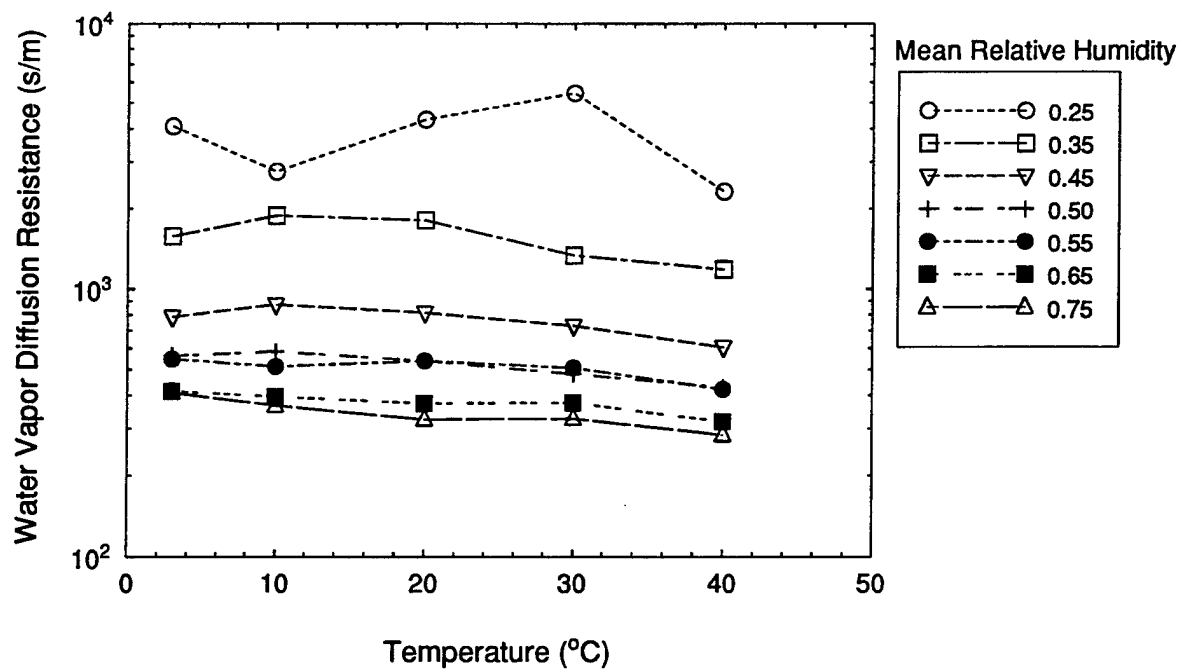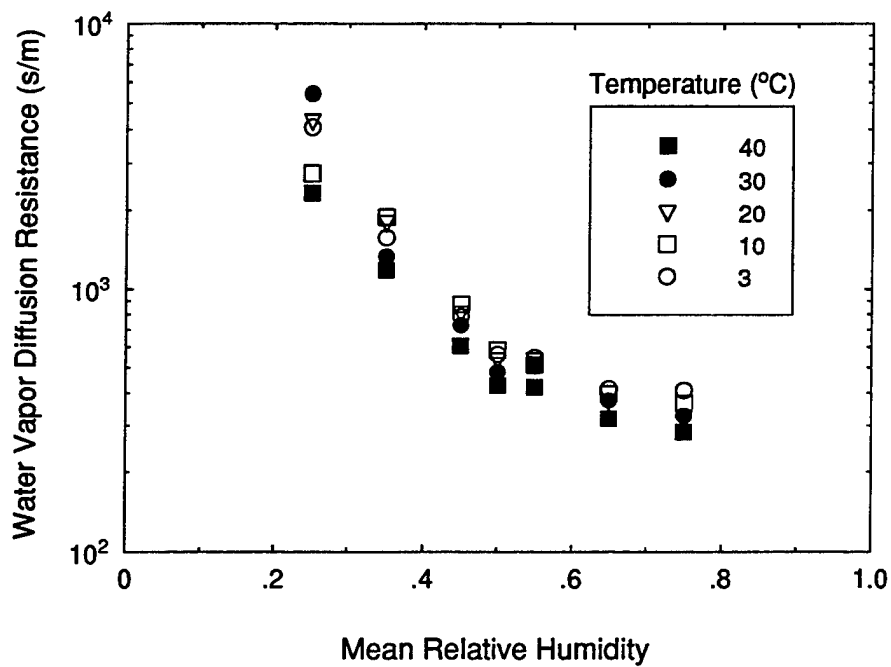

Figure A-18. Effect of Relative Humidity Test Conditions on Water Vapor Diffusion Resistance of Chemical Protective Laminate.

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Appendix B.

Data Tables -- Water Vapor Resistance

Test data for water vapor diffusion resistance (in units of s/m) for the seven setpoints of Table 2, at temperatures of 3, 10, 20, 30, and 40°C. The data in these tables are the total measured resistance, which includes the boundary layer resistance. The intrinsic resistance for each material may be found by subtracting the measured boundary layer resistance at a given temperature.

Measured Boundary Layer Resistances

Temperature (°C)	Water Vapor Diffusion Resistance (s/m)
3	250
10	231
20	219
30	208
40	197

Microporous PTFE Membrane

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
1	0.25	250	242	235	217	212
2	0.35	245	226	222	211	201
3	0.45	258	236	229	218	206
4	0.55	268	243	231	219	203
5	0.65	255	235	221	215	200
6	0.75	277	253	220	209	196
7	0.5	252	237	223	212	201

Perfluorosulfonate Ionomer Membrane

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
1	0.25	369	347	394	415	527
2	0.35	334	280	309	335	413
3	0.45	311	274	280	303	331
4	0.55	313	280	274	283	297
5	0.65	276	264	256	262	260
6	0.75	299	278	254	246	242
7	0.5	285	265	274	281	312

PTFE/PAO/PU Membrane

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
1	0.25	1111	863	868	727	700
2	0.35	1105	690	783	691	653
3	0.45	829	601	618	558	516
4	0.55	683	528	538	488	461
5	0.65	473	407	396	376	358
6	0.75	406	350	324	306	301
7	0.5	669	594	542	478	477

PTFE/PAO/PU Laminate

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
1	0.25	857	945	799	765	732
2	0.35	802	736	750	707	851
3	0.45	702	624	610	605	629
4	0.55	648	526	555	579	560
5	0.65	500	452	428	485	436
6	0.75	453	384	366	404	388
7	0.5	652	596	563	557	572

Polyester/Polyether Membrane

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
1	0.25	847	859	868	817	796
2	0.35	841	709	759	768	804
3	0.45	711	606	630	657	636
4	0.55	617	544	573	603	575
5	0.65	440	410	430	477	439
6	0.75	382	334	339	369	354
7	0.5	603	536	589	561	580

Polyester/Polyether Laminate

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
	0.25	1756	2343	1660	---	1321
2	0.35	1769	1540	1544	---	1614
3	0.45	1473	1216	1154	1030	1142
4	0.55	1221	1104	1083	1079	1041
5	0.65	897	779	795	877	766
6	0.75	679	588	590	662	627
7	0.5	1102	1070	1050	1000	1031

Derivatized Cellophane Membrane

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
1	0.25	2894	2735	3243	3075	2840
2	0.35	2363	1912	2100	1705	---
3	0.45	967	875	897	880	1166
4	0.55	586	536	571	559	648
5	0.65	357	342	345	343	364
6	0.75	330	289	273	254	270
7	0.5	441	450	451	424	542

Derivatized Cellophane Laminate

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
1	0.25	3908	---	4637	5437	3375
2	0.35	4116	---	2795	3205	4192
3	0.45	2626	2726	1834	2172	2190
4	0.55	1614	1698	1533	1846	1756
5	0.65	1072	1153	1058	1210	1127
6	0.75	770	743	704	813	803
7	0.50	1259	1302	1275	1222	1295

Chemical Protective Laminate

Setpoint #	Mean Relative Humidity	Temperature (°C)				
		3	10	20	30	40
1	0.25	4071	2754	4314	5431	2315
2	0.35	1571	1884	1807	1331	1183
3	0.45	786	873	813	728	607
4	0.55	548	514	539	507	421
5	0.65	414	396	373	375	318
6	0.75	408	366	324	327	284
7	0.5	563	584	538	481	428